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Research Article

Preparation and properties of SiC honeycomb ceramics by pressureless sintering technology

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Abstract: SiC honeycomb ceramics with parallel channels and macroporous walls were prepared by combining extrusion molding with pressureless sintering technology in the presence of starch. The extrusion molding constructed honeycomb structure with parallel channels, while the starch formed spherical macropores on the channel walls. The density and bending strength of SiC honeycomb ceramics decreased with the increase of starch content, while the phase compositions did not vary with the starch content. The control in starch addition could adjust the pore structures on the channel walls of SiC honeycomb ceramics.

Keywords: honeycomb ceramic; porous ceramic; silicon carbide (SiC); pore formation

1 Introduction

SiC honeycomb ceramics have attracted considerable attentions owing to its high wear resistance, high corrosion resistance, high coefficient of thermal conductivity, and thermal stability [1–9]. At present, SiC honeycomb ceramics are truly prepared by combining extrusion molding with recrystallization method [1], although some pore-creation processes such as polymeric precursor, and foam template have been developed to prepare SiC porous ceramics. The so-called recrystallized SiC (RSiC) honeycomb is a pure porous SiC material that is produced by heating up shapes consisting of a mixture of bimodal SiC powders at temperatures exceeding 2300 ℃ in a protecting gas atmosphere (Ar). However, the application of RSiC honeycomb is limited by its low mechanical properties (compression strength: 2.5–5 MPa [2]) and high recrystallization temperature. In particular, it is difficult to control the size and distribution of pores in the RSiC honeycomb walls. In our previous research, we have reported the preparation and pore structures of SiC honeycomb ceramics with macroporous walls by using iron oxide as pore former [10].

In this paper, we demonstrate the novel and facile method of preparing SiC honeycomb ceramics by combining extrusion molding with pressureless sintering technology in the presence of starch. The honeycomb structure with 70 cells per square inch and a wall thickness of about 400 μm was obtained by extrusion molding technology, and spherical macropores with a size of 10–30 μm distribute on the channel walls by means of pore-formation of the starch. A lot of benefits are expected to arise from the macroporous structure integrated in the honeycomb ceramics.

2 Experiment

The raw materials of SiC honeycomb ceramics

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included SiC composite powders, starch and additive agents. The SiC composite powders (Taizhou Dongxin Seal Co. Ltd., China) consisted of 90 wt% SiC powders and 10 wt% B_4C (boron carbide, as sintering agent). The starch (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was used as pore-forming agent, and the adding content was designed to be 12.5 wt%, 15 wt%, 17.5 wt% and 20 wt%. The additive agents such as hydroxypropyl methyl cellulose (HPMC, Sigma-Aldrich Co., USA), polyvinyl alcohol (PVA, Sigma-Aldrich Co., USA), oleic acid (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), glycerol (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), and poly(oxyethylene) (PEG 3000, Sigma-Aldrich Co., USA) were used to achieve extrusion molding.

All of the raw materials were mixed by ball milling for 0.5 h, and kneaded by vacuum kneading machine for 3–4 times. The kneaded materials were trapped for 24 h and extrusion-molded to obtain the green bodies with honeycomb structure and parallel channels. After dried at 120 ℃ for 24 h, the honeycomb green bodies were pressureless sintered at 2160 ℃ for 1 h in Ar atmosphere. As a result, the SiC ceramics with honeycomb structure and macroporous walls were prepared.

The bulk density of the sintered samples was measured through the conventional water-displacement method. The three-point bending strength of the sintered samples was performed by electronic universal test machine (CMT5205) with a span of 30 mm and cross-head speed of 0.5 mm/min. The dimension of testing samples is 3 mm × 4 mm × 36 mm, and the testing number of each batch sample is 10. The phase compositions were analyzed by the X-ray diffractomer (XRD, Rigaku D/max-RA). The fracture morphologies of the honeycomb walls were observed by scanning electron microscope (SEM, HITACH S-4800). The pore structure characteristics of macropores in the honeycomb walls were evaluated by mercury porosimetry (Poremaster 60-GT, Quantachrome Instruments, USA).

3 Results and discussion

3.1 Overview of honeycomb ceramics

Extrusion molding The additive agents, such as binders, lubricants, plasticizer, dispersing agents and solvents, are crucial for the extrusion molding of SiC honeycomb ceramics. We choose 5 wt% HPMC and 3 wt% PVA as binders, 5 wt% oleic acid as lubricant, 3 wt% glycerol as plasticizer, and 2 wt% polyethylene glycol and 21 wt% water as solvents. As a result, a smooth flat green body with honeycomb structure and parallel channels can be obtained after the extrusion molding. The green body is dried at 120 ℃ for 24 h to remove the water in the body absolutely.

Sintering The sintering is a vital procedure for the honeycomb ceramics, and the sintering conditions such as temperature, time, atmosphere and heating rate will determine the microstructure and properties of the honeycomb ceramics. We adopt various heating rates in the sintering stage, that is, a slow heating rate of 5 ℃/min from room temperature to 600 ℃, followed by a heating rate of 10 ℃/min from 600 ℃ to 1000 ℃ which can remove the additive agents absolutely. When the heating temperature is in the range of 1000–1800 ℃, a rapid heating rate of 50 ℃/min is performed, and then the heating rate changes to 30 ℃/min in the temperature range of 1800–2160 ℃. The sintering time is 1 h at the sintering temperature of 2160 ℃, and the sintering atmosphere is Ar during the whole sintering stage.

Figure 1 shows the honeycomb channels and macroporous walls of a SiC honeycomb ceramic after sintering. The resultant SiC ceramics have a honeycomb structure with cell channels and macroporous channel walls, although there is little

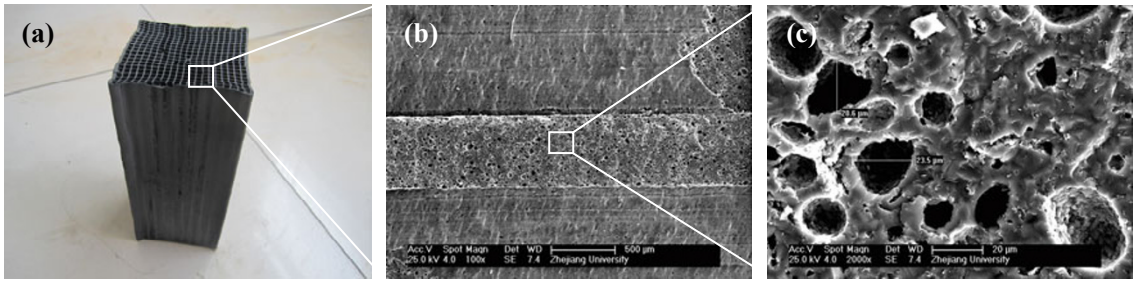

Fig. 1 (a) Honeycomb channels and (b,c) macroporous walls of sintered SiC ceramics.

deformation or shrinkage in the channel walls. A square cell channel shaped in 70 cells per square inch monolith is obtained with a wall thickness of about 400 μm. The amount, size and shape of cell channels are related to the extrusion molds, while the pore structures such as porosity, pore size and pore volume of the channel walls are somewhat different and depend on the pore formation process.

3.2 Sintering and mechanical properties

Figure 2 shows the sintering behaviors of SiC honeycomb ceramics containing different starch contents. With the increase of starch content, the shrinkage ratio of honeycomb sintered body decreases and the mass loss increases, while the density decreases obviously. High mass loss indicates high volatilization of the additive agents and the pore-forming agent. When the starch content increases from 12.5 wt% to 20 wt%, the bulk density of SiC honeycomb ceramics decreases from 2.42 g/cm^3 to 2.20 g/cm^3. The removal of starch will result in a lot of macropores on the walls, which inevitably deteriorate the density of channel walls.

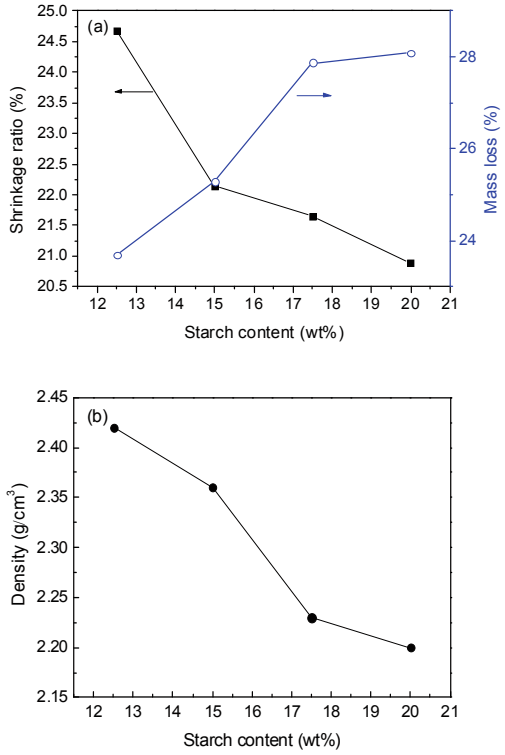

Fig. 2 (a) Shrinkage ratio and (b) density of SiC honeycomb ceramics containing different starch contents.

Figure 3 shows the bending strength of SiC honeycomb ceramics containing different starch contents. The bending strength of SiC honeycomb ceramics obviously decreases with the increase of starch content. The increase in starch content will result in the increase of macropore amount in channel walls, which inevitably deteriorates the mechanical property of SiC honeycomb ceramics. From the load-deformation curve of the honeycomb ceramic with 15 wt% starch, it is seen that the curve shows a slow upward trend with the increase of load, and a relative large peak occurs and keeps for some time when the load reaches a certain level, and then rapidly declines with the further increase of starch content. It indicates that the deformation of honeycomb ceramics is relative slow with the load, which is attributed to the elasticity of honeycomb structure. When the load reaches to a high level, the honeycomb structures will be broken or damaged, resulting in the decline of curve.

3.3 Phase compositions and microstructure

Figure 4 shows the XRD patterns of SiC honeycomb ceramics containing different starch contents. The main crystalline phases include 6H-SiC, 4H-SiC and 2H-SiC, resulting from the SiC composite powders.

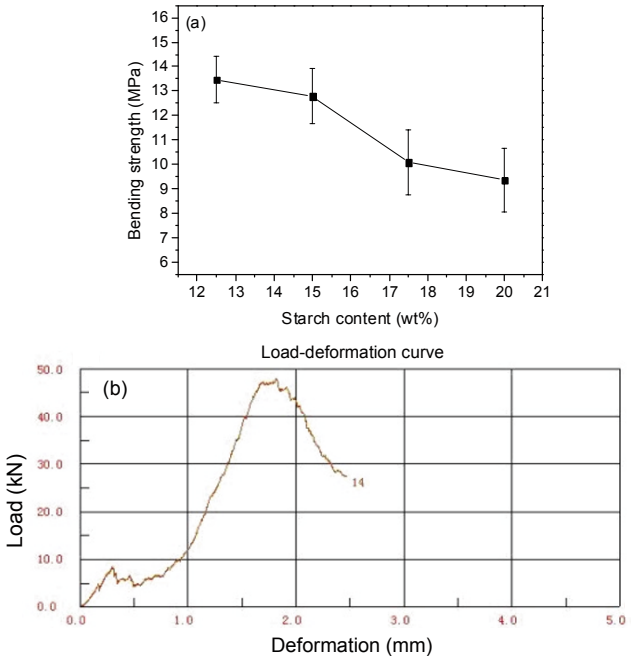

Fig. 3 (a) Bending strength of SiC honeycomb ceramics containing different starch contents and (b) load-deformation curve of SiC honeycomb ceramic with 15 wt% starch.

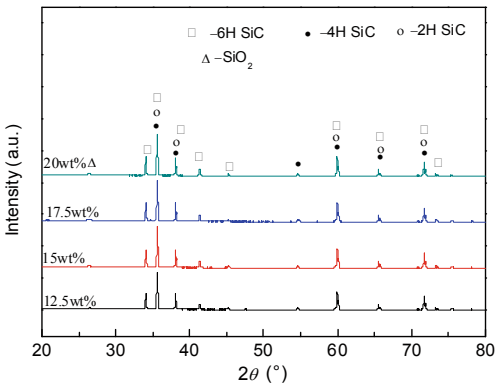

Fig. 4 XRD patterns of SiC honeycomb ceramics containing different starch contents.

The main crystalline phases do not vary with the variation of starch content obviously. It indicates that the pore-forming agent has no effect on the phase compositions of SiC honeycomb ceramics.

Figure 5 shows the SEM images of surface of channel walls at different starch contents. The micrographs provide evidence of open macropores on the channel walls regardless of the starch content. The macropores of the sample are spherical with the size of 10–30 μm at 12.5 wt% of starch. When the starch content increases to 20 wt% and above, the macropore amount increases obviously, and becomes interconnected, while the pore size changes a little with the starch content. These results suggest that the pore structure can be adjusted to some extent by controlling the addition of starch.

3.4 Pore structures

Figure 6 shows the pore size distributions determined by mercury porosimetry for the channel walls at different starch contents (15 wt%, 17.5 wt% and 20 wt%). The cumulative pore volume is relatively low and the pore size distribution is a little wide and flat at 15 wt% of starch, which do not change much at 17.5 wt%. It indicates that most of created macropores in the two samples are still closed or isolated, although the two samples seem to have a lot of open macropores as shown in Fig. 5. When the starch content increases to 20 wt%, the sample possesses a sharp pore size distribution, and the pores are distributed roughly between 0.08 μm to 0.4 μm, which is much lower than the pore size (10–40 μm) of RSiC honeycomb walls. It indicates that some small interconnected pores with a regular shape distribute on the large isolated macroporous interiors.

Figure 7 shows the median pore size and porosity of channel walls at different starch contents (15 wt%, 17.5 wt% and 20 wt%). The median pore size and porosity of the samples increase with an increase starch content. The median pore size and porosity increase from 105 nm and 19.8% to 220 nm and 37% respectively, when the starch content increases from

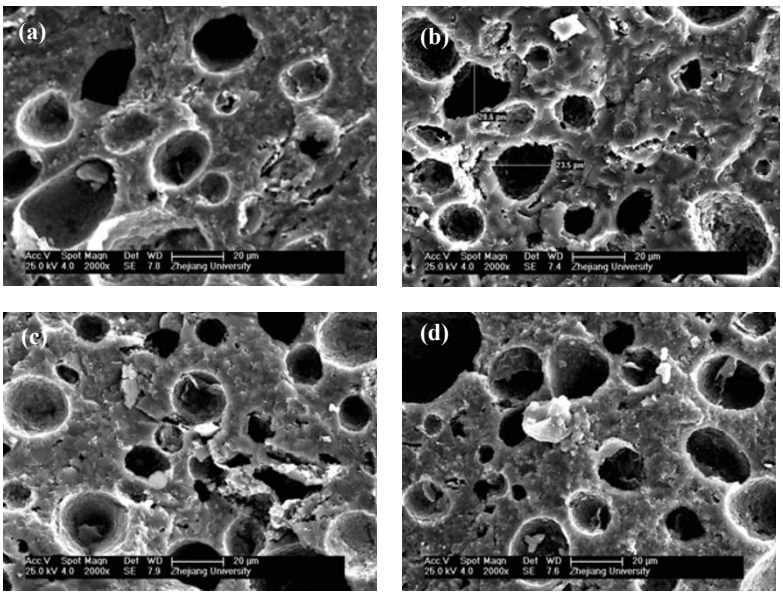

Fig. 5 SEM images of surface of channel walls at different starch contents: (a) 12.5 wt%, (b) 15 wt%, (c) 17.5 wt%, (d) 20 wt%.

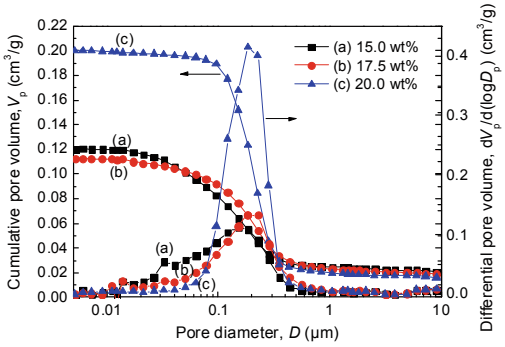

Fig. 6 Pore size distributions determined by mercury porosimetry for the channel walls at different starch contents: (a) 15 wt%, (b) 17.5 wt%, (c) 20 wt%.

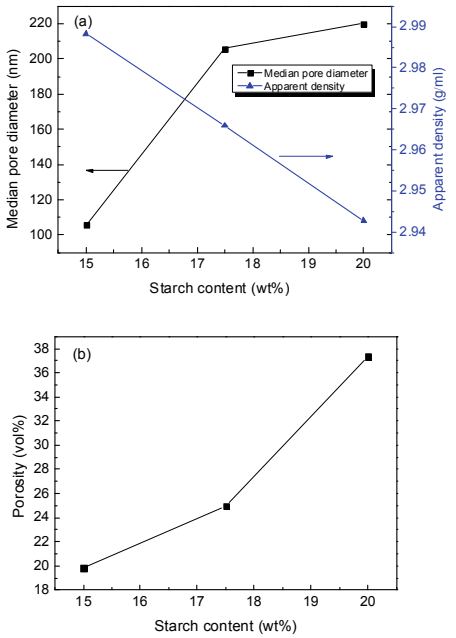

Fig. 7 (a) Median pore size and (b) porosity of channel walls for SiC honeycomb ceramics containing different starch contents.

15 wt% to 20 wt%. The increase in porosity and pore size with increasing starch content is attributed to the increased mass loss of the specimens as shown in Fig. 1 and the removal of pore-forming agent.

4 Conclusions

SiC honeycomb ceramics with macroporous walls were prepared by pressureless sintering technology. The extrusion molding constructed the honeycomb structure with 70 cells per square inch and a wall thickness of about 400 μm, while the starch as pore-forming agent formed spherical macropores with a size of 10–30 μm on the walls. The pore formation of starch on the channel walls weakened the bulk density and bending strength of honeycomb ceramics, while did not change the phase compositions. The SiC honeycomb ceramic containing 20 wt% starch had a macrostructure consisting of large spherical macrospores and small interconnected pores in interiors, with a porosity of 37%. The honeycomb ceramics with macroporous walls are promising for wide applications such as filtration, separation, catalysis and so on.

Acknowledgements

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